STUDIES ON BENZO[g]CYCL[3.2.2]AZINE DERIVATIVES

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Recently there has been considerable effort in trying to rationalize the effects of benzo-fusion on aromatic annulenes. There is also interesting of the rational effects of benzo-fusion on cycl[3.2.2]azine (1).

Now, we wish to report the synthesis of benzo[g]cycl[3.2.2]azine (2) and benzocyclazine derivatives (3, 4, 5, 6). The [2+8] cycloaddition reaction of 7 with dimethyl acetylenedicarboxylate (DMAD) in the presence of a 5% palladium-on-charcoal as dehydrogenation catalyst under refluxing 30 h in xylene gave 3, followed by hydrolysis and decarboxylation to give 4. In a manner similar to the above method, the reaction of 8 with DMAD gave 5 and 6. The desulfurization of 5 with Raney-nickel easily occurred to give 9. Hydrolysis of the diester with 10% sodium hydroxide proceeded essentially quantitatively to give the diacid 10. Finally, decarboxylation of the diacid using copper chromite in quinoline occurred smoothly to produce the desired benzo[g]cycl[3.2.2]azine (2).

The benzocyclazine (2) has a sweet look like the naphthalene and a stable crystaline as bright yellow leaflets which are obtained analytically pure after recrystallization from methanol, mp 141°C. In the ^{1}H-NMR spectrum the peripheral protons are shown in the range δ:7.37-8.23 for the protons of the cyclazine ring and δ:7.62-8.67 for the benzo ring. Thus the effect of benzo fusion is to shift the peripheral protons downfield relative to the cycl[3.2.2]azine (1), implying no reduction in ring current as expected. Their chemical shifts are similar to the aceanthrylene.